Equilibrium of urea-water system, I : the relation between equilibrium pressure and temperature

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EQUILIBRIUM OF UREA—WATER SYSTEM, I.

The relation between equilibrium pressure and temperature.

By Ryo Kiyama and Hideo Kinoshita*.

Introduction.

Upon the reference to the equilibrium pressure of urea synthesis, it was reported as the decomposition pressure or equilibrium pressure of ammonium carbamate by Krase[1], Tokuoka[2][3][4], Egan[5], Briner[6], Matignon and Frejacques[7], and Kitawaki[8]. But they are all below 150°C except 194.1°C of Kitawaki. It is well known that the yield of urea change by packing ratio g/cc, remembering that the equilibrium pressure are not coincident among experimenters, the authors studied that the equilibrium pressure is also changed by packing ratio in the field of the higher temperature range, 130°C~240°C. The equilibrium pressure and the yield of urea are measured at the time of 3~24 hours and at the packing ratios of 0.1~0.9 g/cc.

Apparatus.

The apparatus is constructed with a reaction vessel, a pressure gauge and a high pressure valve, are connected with a steel pipe of 10 mm O.D and 3 mm I.D. The Bourdon type pressure gauge, inhaled lubricant oil, is protected by a U-type steel stem pipe filled with mercury from corrosion and the high pressure valve is adapted at the branch of the gauge stem pipe near the reaction vessel. The authors used three types of reaction vessels, (A) Ni-Cr steel, capacity 28 cc, (B) admitted a glass vessel in A, and (C) 1 mm thickness silver lining in a mild steel vessel, capacity 50 cc.

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1) N. W. Krase and V. L. Gaddy, *Ind. Eng. Chem.* **14**, 611 (1922)
2) M. Tokuoka, *J. Agr. Chem. Japan*, **10**, 1333 (1934)
3) " *ibid.* **11**, 107 (1935)
4) " *ibid.* **11**, 174 (1935)
5) E. P. Egan, *Ind. Eng. Chem.*, **38**, 454 (1946)
6) E. Briner, *J. Chim. Phys.*, **4**, 266 (1906)
7) C. Matignon and Frejacques, *Bull. Soc. Chim.*, **31**, 394 (1922)
8) I. Kitawaki, S. Hori and Y. Shimoda, *Bull. Gov. Chem. Ind. Res. Inst. Tokyo*, **32**, No. 6 & 10 (1937)

The Review of Physical Chemistry of Japan Vol. 21 No. 1 (1950)

Sample and experimental method.

The purity of urea, 99.9%, obtained by recrystalization is used. As to the experimental method, after suppiying the calculated urea in the reaction vessel, fixed the all co nections, silver packing 1 mm thickness is used for preventing the leak at cooling. The air in the reaction vessel is pumped out and added the water in the reaction vessel by the definite mol ratio of urea and water, thro gh the high pressure valve. The apparatus is set in the electric furnace, except the pressure gauge. Temperature is measured by a thermocouple inserted in wall or inner of the reaction vessel. Time for reaching the reaction temperature is about 1.5～2 hours. The reaction vessel is cooled in ice water at the end of the reaction, and the co tents are analysed. The residual urea is decided by the following method. After oxidizing the corroded iron, filtering, and vaporizing water by evac ation at 65°C, the deposited urea is directly weighed. The existence of biuret is neglected by the low temperature treatment.

Experimental results.

(I) Relation between the equilibrium pressure, temperature and time.

(1) Relation between the equilibrium pressure and time.

The pressure change is measured in the container C refering to time 7～24

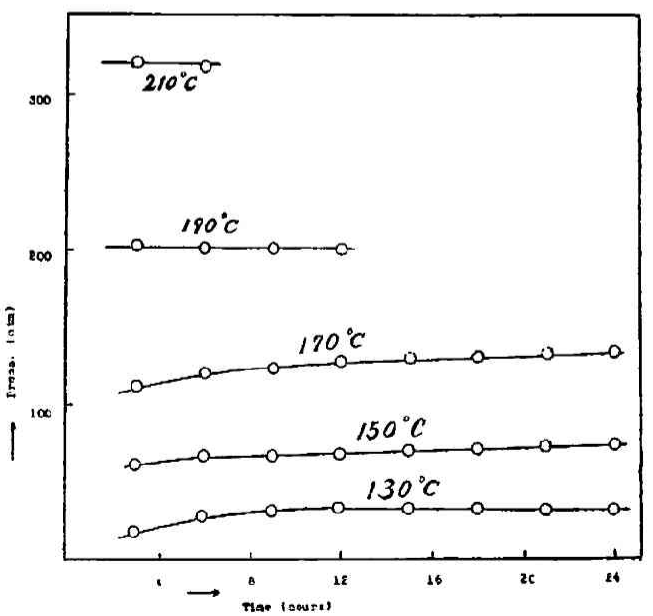

Fig. 1 Pressure—time curves. (0.78 g/cc)

The Review of Physical Chemistry of Japan Vol. 21 No. 1 (1950)

hours for the experiments of temperatures 130, 150, 170, 190, 210°C, packing ratio 0.78 g/cc. These results are illustrated in Fig. 1.

(2) Relation between the equilibrium pressure and the temperature.

The equilibrium experiments of temperatures 130, 150, 170, 190, 210, 230, 240°C are performed in the containers A and B. Time above 190°C is 3 hours and below 170°C is 7 hours. The results are shown in Table 1. In Fig. 2, the authors compared their results with the data of Matignon and Frejacques, Egan, Tokuoka and Kitawaki.

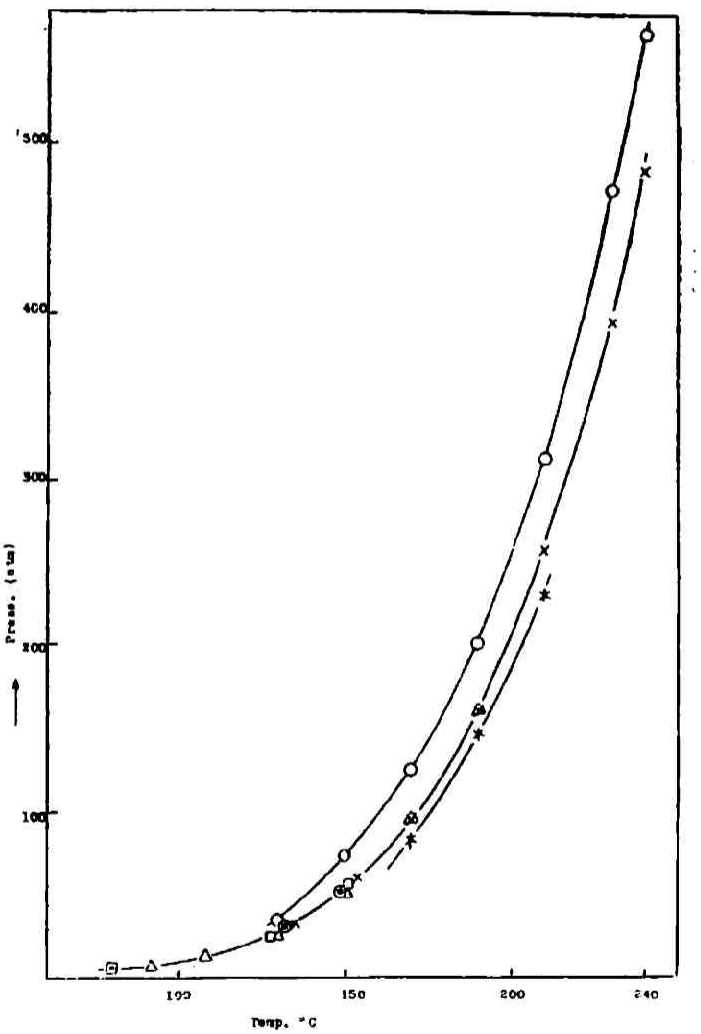

Fig. 2 Pressure—temperature curves.

observer	condition		
○ authors	0.676 g/cc,	△ Kitawaki	
× authors	0.5 " ,	□ Tokuoka	0.9 g/cc
✳ authors	0.3 " ,	⊙ Matignon & Frejacques	
		⊡ Egan	

The Review of Physical Chemistry of Japan Vol. 21 No. 1 (1950)

Table 1

Packing ratio, g/cc	Container	Temperature, °C							Observer
		130	150	170	190	210	230	240	
0.676	A	34	73	125	200	310	470	563	authors
0.5	B	28	56	97	161	256	391	491	authors
0.3	B			83	148	230			authors
—	glass	28.8	54	97	163				(8)
0.9	Sn	28.4	56						(4)
—	glass	28	55.1						(7)

(11) Relation between the temperature, rate of decomposition and time.

At the same time the measurements of the temperature and the residual urea of liquid phase at the definite time interval in the container is measured, and the results are shown in Fig. 3.

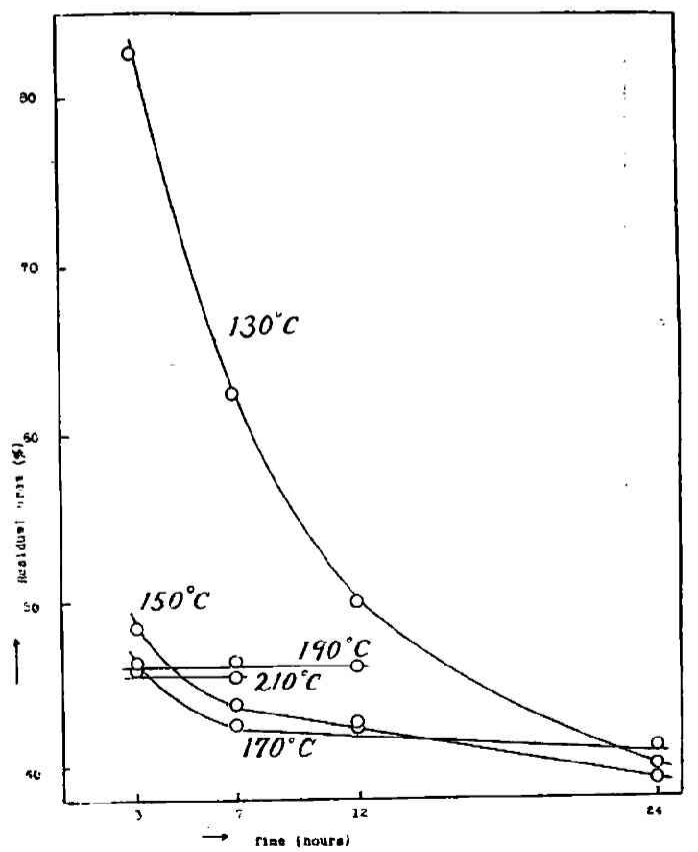

Fig. 3 Residual urea—temperature curves. (0.78 g/cc)

The Review of Physical Chemistry of Japan Vol. 21 No. 1 (1950)

Considerations.

(I) The equilibrium pressure. It seems that that the equilibrium pressure is charged by packing ratio as shown in Fig. 2, is due to the difference of solubility of ammonia and carbon dioxide to the liquid phase. Consequently the composition of gas phase is related to pressure change, but will be explained in detail in the next report. When the temperature is below 170°C, pressure can not reach equilibrium at the experiments of 24 hours (the containers B and C). There may be the influence of hydrogen, produced by corrosion of the steel pipe which is in contact with gas phase. But this view is not applicable for the fact that the pressure can reach equilibrium in short time, when the temperature is above 190°C. Moreover, there is the same tendency in the curve of pressure-time and residual urea-time, and when the temperature is below 170°C, the residual urea can not reach equilibrium after 24 hours. Accordingly, though the reaction of ammonium carbamate to urea is fast[8], the decomposition of urea is very slow and the pressure does not reach any real equilibrium pressure below 170°C.

There exists the residual pressure when the reaction vessel is cooled in ice water after the reaction is over. The residual pressure is confirmed due to hydrogen by corrosion and carbon dioxide. The volume of hydrogen corresponds to corroded iron. Consequently, it is expected that carbon dioxide is in excess in gas phase after the long run of cooling because the solubility of ammonia is greater than carbon dioxide. This is against Tokuoka's idea[9].

The volume of hydrogen at the temperatures of 130, 150, 170, 190, 210°C, after 3 hours, with packing ratio 0.676 in the A container is shown in Table 2.

Table 2

Temp. °C	Volume of hydrogen, cc
130	0.4
150	4.9
170	19.9
190	38.4
210	82.8

Upon the relation of equilibrium pressure and temperature, the following experimental equations are presented because of the linear relation between the logarithm of pressure and the reciprocal of the absolute temperature. The existence of the relation of straight line in the case where the packing ratio is 0.676 and 0.5 is confirmed. It is expected that the gas phase in equilibrium of urea-water system consists of carbon dioxide, ammonia, water and urea, but the physical meaning of the existence of this relation is not clear in the present paper.

$$\log P = -2346.58/T + 7.2789 \quad \text{(Kitawaki)}$$

$$\log P = -2741.9/T + 8.2680 \quad \text{(Egan)}$$

$$\log P = -2146.00/T + 6.936 \quad \text{(authors 0.676 g/cc)}$$
$$\log P = -2211.69/T + 6.989 \quad \text{(authors 0.5 g/cc)}$$

(II) The residual urea. The maximum residual urea is 190°C, but it is expected that the maximum of urea also depends on packing ratio. In Table 3, the authors compare their data with the literature.

Table 3

Temp. °C	Time hrs	Packing ratio g/cc	Urea %	Initial	Container	Observer
130	178	0.65	40.1	carbamate	glass	(8)
"	64	.9	40.7	"	Sn	(2)
"	24	.5	33.6	"	glass	(7)
"	"	.78	39.9	urea + water	silver	authors
150	"	.65	44.5	carbamate	glass	(8)
"	30	.9	44.9	"	Sn	(2)
"	4	.49	44.6	"	glass	(7)
"	24	.9	45.8	urea + water	steel	(9)
"	"	.95	44.8	carbamate	"	(9)
"	"	.78	39.5	urea + water	silver	authors
170	"	.65	45.6	carbamate	glass	(8)
"	"	.9	47.7	urea + water	steel	(9)
"	"	.94	47.9	carbamate	"	(9)
"	"	78	41.0	urea + water	silver	authors
190	"	.65	45.3	carbamate	glass	(8)
"	"	.92	49.8	urea + water	steel	(9)
"	"	.97	49.6	carbamate	"	(9)
"	12	.78	45.8	urea + water	silver	authors

Conclusions.

(I) The equilibrium experiments that started from the urea-water system at the temperature range 130~240°C and packing ratios 0.78, 0.676, 0.5 0.3 g/cc are performed.

(II) The decomposition of urea is very slow below the temperature of 170°C and can not reach equilibrium after 24 hours, but above the temperature of 190°C, equilibrium reaches in a few hours.

(III) When the iron reaction vessel is used, hydrogen is produced by corrosion and that volume corresponds to corroded iron.

(IV) The residual pressure in cooling is due to hydrogen by corrosion and

9) K. G. Clark, V. L. Gaddy and C. E. Rist, *Ind. Eng. Chem.*, **25**, 1092 (1933)

The Review of Physical Chemistry of Japan Vol. 21 No. 1 (1950)

excess carbon dioxide.

(V) There exists the relation of straight line between log P and 1/T.

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